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Publication Date

2017-11-01

DOI

10.1016/j.jnucmat.2017.09.007

Peer reviewed

Effect of Technetium-99 Sources on Its Retention in Low Activity Waste Glass

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Abstract

Small-scale crucible melting tests on simulated waste glass were performed with technetium-99 (Tc-99) introduced as different species in a representative low activity waste simulant. The glass saw an increase in Tc-99 retention when $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and various Tc-minerals containing reduced tetravalent Tc were used compared to tests in which pertechnetate with heptavalent Tc was used. We postulate that the increase of Tc retention is likely caused by different reaction paths for Tc incorporation into glass during early stages of melting, rather than the low volatility of reduced tetravalent Tc compounds, which has been a generally accepted idea. Additional studies are needed to clarify the exact mechanisms relevant to the effect of reduced Tc compounds on Tc incorporation into or volatilization from the glass melt.

1 Introduction

Radioactive wastes present at the U.S. Department of Energy's Hanford Site will be vitrified at the Hanford Tank Waste Treatment and Immobilization Plant (WTP). Tank wastes

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will be combined with glass-making additives in a slurry mixture called the feed, which is fed into melters, and cooled into glass. Technetium-99 (Tc-99) is one of the more challenging radionuclides present in Hanford low activity waste (LAW) because of its long half-life of 2.13×10^5 year and its penchant to become water-soluble pertechnetate. The pertechnetate ion (TcO_4^-), a stable form of oxidized Tc, is highly mobile in oxidized aqueous conditions and volatile at the temperatures of waste processing in glass melters [1, 2], thus inhibiting Tc incorporation into the product glass [3-5].

As currently planned, volatilized Tc will be captured in an off-gas system, recycled back to pretreatment, and eventually re-added to the glass melter [6]. This recycling also returns sulfur and halides to the glass melt, which can limit the waste-loading of the glass [7]. Methods of increasing the fraction of Tc incorporated into and retained in the glass (referred to as “retention”) to avoid recycling are preferred, and several avenues of research are addressing this area [5, 7, 8].

A possible solution is the capture of Tc either from liquid waste streams or from off-gas condensates by incorporation into a durable mineral phase. For example, a mineral-forming precursor could be added directly into waste streams before being fed to the melter, or to the off-gas condensate. If the thermal stability and chemical durability of the selected mineral are sufficient, incorporated Tc may remain within the mineral structure through melting of the glass, thus inhibiting Tc volatility [9]. If used in the off-gas system, the resulting Tc mineral (not containing sulfur or halides) could be recycled back to pretreatment, serve as a standalone waste form, or be incorporated into a low-temperature waste form that is being considered for immobilizing secondary wastes from the WTP [10, 11].

Minerals such as perovskite [12], pyrochlore [12, 13], spinel [14], and sodalite [15-17] have been shown to incorporate Tc, and are therefore potentially suitable for this use [18]. Rhenium (Re) is used as a Tc surrogate due to the similarities of the pertechnetate and perrhenate species, and Re-containing sodalite (with Re^{7+}) has demonstrated the utility of using a durable mineral phase to increase Re retention in glass [9, 15]. However, attempts to synthesize minerals, such as spinel that can incorporate tetravalent Tc, with tetravalent Re were not successful, presumably because of differences in ionic size and redox potential. While Re is a widely used chemical surrogate for Tc [2] that behaves similarly in heptavalent oxidation states, the redox potentials and mechanisms of Tc and Re are not similar.

The retention, partitioning, and oxidation of Tc in feeds prepared with different Tc-bearing minerals as well as TcO_2 were compared against KTcO_4 -spiked feed. Two standard solutions— KTcO_4 and $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ —and four Tc-doped iron minerals—Tc-trevorite from $\text{Fe}(\text{OH})_2$, Tc-magnetite from $\text{Fe}(\text{OH})_2$, Tc-goethite, and Tc-trevorite from co-precipitation—were prepared and tested in melts of LAW simulant glasses formed at a series of temperatures. Both inductively coupled plasma mass spectrometry (ICP-MS) and liquid scintillation counting (LSC) were performed to measure Tc retention of all feeds and heat-treated samples. Leach tests were performed to characterize the fraction of Tc in the soluble and insoluble phases of the feed and glass-forming melt. X-ray absorption near edge spectrum (XANES) analysis was performed to characterize the oxidation state of the Tc in the samples. The effects on Tc during melting are discussed, and mechanistic explanations for these observations are offered.

2 Preparation of Tc-99 source materials

2.1 *KTcO₄ standard solution*

The KTcO₄ standard solution was prepared as described by Soderquist et al. [19] for doping glass with a control Tc source. Ammonium pertechnetate was dissolved and recrystallized to ensure purity, and then dissolved in K₂CO₃ solution and slowly evaporated, driving off ammonium carbonate was driven off during evaporation, leaving KTcO₄. The KTcO₄ was weighed and dissolved in water to create a spike solution of known Tc concentration. Aliquots of this spike solution were added to feeds as necessary using a pipette.

2.2 *TcO₂·2H₂O standard solution*

The TcO₂·2H₂O was prepared by hydrolysis of (NH₄)₂TcCl₆ in water, as described in Rard et al 1999 [20]. Dry (NH₄)₂TcCl₆ was dissolved in water and then warmed to near boiling with dry N₂ (g) blown over the surface. The solution was evaporated nearly dry to expel HCl produced by hydrolysis. The mixture was re-suspended in water and re-evaporated several times to eliminate residual HCl. Hydrolysis was judged to be complete when the hydrous TcO₂ settled under gravity and left clear supernatant. The hydrous TcO₂ product was centrifuged, washed with water to remove ammonium chloride, and finally dried at ~120°C under N₂ (g).

2.3 *Tc-trevorite from Fe(OH)₂*

Tc-trevorite was prepared as described by Lee et al. 2016 [21]. Five milliliters of a 0.5 M NiCl₂ solution and 0.09 g of Fe(OH)₂ powder were added to a vial and shaken for 24 hours, after which 15 mL of a solution of 0.001 M NaTcO₄ and 1 M NaOH was added. The combined solutions were heated at 75°C for 72 hours. All solutions were anoxic, and work was performed in an anoxic glove box. After the heat treatment, the reacted material was removed from the

hood and rinsed over a 0.45 μm filter. A scanning electron microscopy (SEM) micrograph of the Tc-trevorite is shown in Figure 1. Based on SEM micrographs of the particles, particle sizes were estimated to be 400 to 600 nm.

2.4 Tc-magnetite from $\text{Fe}(\text{OH})_2$

Tc-magnetite was prepared as described by Um et al. [22] in a manner similar to the Tc-trevorite from $\text{Fe}(\text{OH})_2$. To synthesize the magnetite, NiCl_2 was excluded, and the $\text{Fe}(\text{OH})_2$ was reacted with the NaTcO_4 and NaOH for 72 hours, without the initial 24 hour reaction with NiCl_2 . Results from XRD analysis showed impurities of goethite (see **Error! Reference source not found.**).

2.5 Tc-goethite

Tc-goethite was prepared as described by Um et al. [23]. Powdered goethite was suspended in a pH <2 HNO_3 solution. Powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.48 g) was directly added to the goethite slurry as a Fe(II) source, and the mixture was reacted for 1 day in an anoxic chamber. Then, NaTcO_4 solution was added in 0.1M of NaOH solution and homogenized by shaking for 1 to 2 days before mixing with goethite slurry. After mixing, additional $\text{Fe}(\text{NO}_3)_3$ was added to “armor” (i.e., precipitate an additional goethite layer upon) the goethite and continuously reacted at 80°C for 7 days. The final Tc-goethite was rinsed, filtered, and dried in air before use. A micrograph of the Tc-goethite is provided in Figure 2. Based on the image, the goethite particles are approximately 1 μm by 200 nm.

2.6 Tc-trevorite from coprecipitation

Tc-trevorite particles were prepared using an aqueous mineralization of FeSO_4 , NiCl_2 , and pertechnetate as described by Lukens et al. [24]. The compounds were dissolved in

deionized water that was first sparged with N_2 (g) and then added to a 2 M NaOH/ $NaNO_3$ solution that was finally heated to 95°C for 90 minutes. Several rinses and centrifuging steps made the sample ready to use. XRD analysis presented in supplemental information of [24] indicate crystallite size of 28 nm.

3 Glass feed preparation

Low activity waste glass AN-102 was used as a test glass in continuity of research by Jin et al. 2015, following the recipe prepared by Matlack et al. 2011 [5, 25]. The composition of AN-102 glass feed to make 1 L of slurry is shown in Table 1. [25]. The feed slurry was batched in 17.5 g amounts which were used for three 5-gram heat treatments, leach test, and XANES analysis. Table 1 shows the batching followed for tests used. The agate-milled powder components and the dissolved simulant portion were mixed together and sub-divided into Teflon[®]™ beakers. Various Tc sources were added to each beaker and the mixture (i.e., the feed) was stirred briefly. The beakers were then placed in a drying oven (usually overnight) at 105°C. The dried feeds then were milled for 5 minutes in an Al_2O_3 ball mill to ensure homogeneity of the final feed.

The Tc concentrations of the trevorite and magnetite sources were ascertained by measuring the Tc concentration of the solutions in which they were synthesized. The Tc concentrations of the solutions were measured after synthesis by ICP-MS and LSC, with Tc lost from solution assumed to be in the mineral product. In the case of the goethite, measurement of the Tc concentrations of both the synthesis solution and the goethite after acid digestion were made by ICP-MS [26]. Finally, the Tc concentrations of the TcO_2 and $KTcO_4$ solutions were estimated gravimetrically from the dry weight of $KTcO_4$ used to prepare the sources.

KTcO₄ was added to approximate a concentration of 100 ppm Tc in glass, while other test materials were added to the extent they were available. The Tc content of each dried feed was directly measured by LSC, which was used as the baseline to calculate Tc retention for each sample. To measure experimental uncertainty, a duplicate batch of KTcO₄ feed was prepared from raw materials, heat-treated, and analyzed in triplicate.

4 Experimental Procedure

4.1 Heat treatments

Once a dried, powdered feed was prepared, 5.0 g samples were placed in Pt-Rd crucible and into a Deltech furnace at ~20 °C. The furnace was powered on and heated to ~150°C. After reaching 150°C, the temperature was programmed to increase at a rate of 5°C min⁻¹ to target temperatures of 600, 800, or 1000°C. When the furnace reached the target temperature, it was powered off and allowed to cool to room temperature. This treatment is different than heat treatment carried out on Re-containing AN-102 glass by Jin et al. 2015 [5], where samples were air quenched. As a consequence, samples in the present test underwent heating slightly longer, taking perhaps an hour to cool below 400°C. Once cool, the samples were removed from the furnace, weighed, and removed from the crucible. Whole samples were then pulverized in the alumina ball mill for 5 minutes to ensure homogeneity.

To evaluate the uncertainties of the experiments in this study, duplicate or triplicate tests or analyses were performed for selected conditions and samples. Two batches of AN-102 feeds spiked with 100 ppm KTcO₄ were prepared separately. The original KTcO₄ feed batch was used for the full of heat treatment series while a duplicate feed batch was heat-treated to

1000°C in triplicate by placing all three samples contained in separate Pt-Rd crucibles into one furnace.

4.2 Weight Loss Correction

Weight loss from evolved gases occurs as feed is heated and transitions into glass. The results of chemical analyses for Tc concentration in heat-treated samples were corrected for this weight loss in order to account for Tc concentrations in all samples. The weight-loss factor is the ratio of the mass of heat-treated sample to the mass of dried feed used for heat treatment. The weight-corrected Tc concentration normalized to the starting concentration in dried feed is calculated by multiplying the as-measured Tc concentration in heat-treated sample by the weight-loss factor. Then, Tc retention is the ratio of weight-corrected Tc concentration in a heat-treated sample to the Tc concentration in the dried feed.

4.3 Chemical analyses

NaOH fusion of the dried feed and heat-treated samples was performed to prepare the samples for LSC determination of the Tc concentration. Preparation involved placing ~50 mg of each sample into Ni crucibles, adding 2.5 mL of 20 wt% NaOH solution, and mixing the contents. The crucibles were heated on a hot plate to ~450°C at which point the water had evaporated and the NaOH had become a liquid flux and dissolved much of the solid sample. After cooling, the NaOH and remaining solids were transferred into a 50 mL centrifuge tube and washed with water. After centrifuging, the supernatant was set aside. The Ni crucibles were rinsed into the centrifuge tube containing the remaining solids with 1 mL of concentrated HNO₃ and several milliliters of water rinses after which only a residue presumed to be undissolved ZrSiO₄ remained in the centrifuge tubes. This undissolved ZrSiO₄ was present in the dried feeds and

samples heated to 600°C, but not present in samples heated to higher temperatures. The HNO₃ solution and previous supernatant were combined, adjusted to pH 1-3 with dilute HNO₃, and diluted to 45 mL final volumes with deionized water.

For LSC analyses, a 0.5-mL aliquot of each sample was transferred to a LSC vial and combined with 15 mL of LSC cocktail. ZrSiO₄, when present, was transferred to a separate LSC vial, suspended in 15 mL of LSC cocktail, and counted as well (all counts from ZrSiO₄ residue were less than 1% of the total for analyzed samples). A Packard Instruments TriCarb® 3100TR was used for LSC for Tc analyses. Counts were recorded from the 0 to 300 keV regions, which captures ⁹⁹Tc 294 MeV β energies. Total counts then were normalized by the exact weight of the sample fused, and the concentrations of the dilution and 0.5 mL added to the LSC vial to give concentration of Tc in each sample.

For selected samples, ICP-MS was used to determine Tc concentration in solid samples after microwave-assisted digestion as described by Lee et al. [21]. A set of the same selected samples also was submitted to Southwest Research Institute (SwRI) for Tc concentration determination by ICP-MS after KOH fusion similar to Re analyses described in previous studies [5, 27].

4.4 Leach tests

Leach tests were performed to determine the fraction of water-soluble Tc in the dried feed and the samples heat-treated to 600 and 800°C. Based on the results of previous leach tests by Jin et al. [5], It was assumed that there was a negligible soluble phase, and therefore no water-soluble Tc, remaining after heat treatment to 1000°C. For the samples tested, 0.3 g of each was added to a 15 mL centrifuge tube, and 14 mL of room-temperature deionized water

was added. The centrifuge tubes were inverted and shaken manually for 50 minutes, and then centrifuged at 3000 RPM for 6 minutes. This procedure provided approximately an hour of contact between the solids and water. This extended leaching period was chosen because the 10 minutes of leaching with room temperature water used by Jin et al. [5] was not aggressive enough for some samples. After leaching, the supernatant was pipetted off the compacted solids and saved as the “leach” supernatant. The centrifuged solids were rinsed with 14 mL of deionized water, and then the tubes were vigorously shaken to combine the water and solids. The tubes were then centrifuged a second time, and the second supernatant was pipetted off and saved as the “rinse” supernatant. Dilute HNO_3 was added to each supernatant to reduce the pH to within the 1 to 3 range. A 0.5 mL aliquot of each pH-adjusted supernatant was transferred to a LSC vial, combined with 15 mL of LSC cocktail, and counted on the LSC instrument as described above. The sum of the activities for the supernatants is the total soluble fraction of Tc in each sample. Residual solids remaining after the leaching steps were dried in the drying oven at approximately 100°C and weighed to determine the mass fraction of the sample that was water soluble.

4.5 XANES analysis

XANES analysis was carried out using the Stanford Synchrotron Radiation Light source to collect the data at room temperature, as in Lukens et al [24]. Approximately 0.5 g portions were taken from each feed and selected heat-treated sample and taped inside Teflon[®]TM sampled holders using Kapton tape. X-rays were mono-chromatized using a double crystal monochromator with Si 220 crystals. The second crystal was detuned by 70% to reduce the harmonic content of the beam. Intensities of the incident and transmitted x-ray beam were

measured using N₂ (g)-filled ion chambers. Fluorescence data was obtained using a Canberra 100 element Ge detector; for the magnetite samples, two layers of aluminum foil were placed in front of the detector to reduce the intensities of the Fe fluorescence lines. The data were corrected for dead time effects. Data were averaged using the software package SixPack as described by Lukens et al. [28].

Initially, XANES analyses were performed for all dried feed and heat-treated samples for the KTcO₄, Tc-goethite, and Tc-magnetite feeds. Subsequently for the remaining samples, XANES was performed for the dried feed and 600°C samples only because the samples that were measured indicated that Tc⁴⁺ oxidized rapidly after 600 °C. All Tc retained in the 800 and 1000 °C samples was assumed to be Tc⁷⁺. Sharply decreasing amount of Tc⁴⁺ from feed to 600 °C samples demonstrate this trend. .

5 Results

Table 2 summarizes Tc concentrations before and after heat treatment to 1000°C, weight-loss factor, and Tc retention in all four 1000°C KTcO₄-spiked samples. The relative standard deviation (RSD) was calculated from the four measurements as an estimate of reproducibility for Tc concentrations in the feeds and heat-treated samples and given in Table 2.

Table 3 and **Figure 3** compare the Tc concentrations in two dried feed samples (goethite and KTcO₄ feeds) and one heat-treated sample (KTcO₄ heated to 1000°C) obtained by three different analytical techniques: LSC after NaOH fusion, the primary technique used in this study; ICP-MS after microwave-assisted digestion; and ICP-MS after KOH fusion (performed at SwRI). The RSD values given in Table 2 were used to calculate the standard deviations of LSC results for

the KTcO_4 feed and 1000°C heat-treated samples as given in Table 3. The standard deviations are generally slightly smaller than the differences between LSC and two set of ICP-MS results (see Figure 3), which suggests that there may be minor analytical biases. The discussion in this study is based only on the LSC measurements.

Table 4 summarizes the Tc concentrations in dried feed and heat-treated samples (weight corrected for heat-treated samples), weight-corrected Tc concentrations in leach solutions of dried feed and heat-treated samples, weight-loss factors, and calculated Tc retentions in heat-treated samples. Table 4 also includes the results of XANES analysis showing the fractions of Tc^{7+} and Tc^{4+} found in each sample.

Figure 4 shows the fraction of total Tc added to the feed retained in soluble and insoluble phases of the dried feed and heat-treated samples (in short, “fraction of soluble/insoluble Tc”) as a function of temperature. The fraction of soluble Tc was calculated by dividing the weight-corrected Tc concentration in leach solution by the Tc concentration in dried feed, which represents the fraction of total Tc that was present in dried feed and then remained in soluble phase of each sample after heat treatment. The fraction of insoluble Tc was obtained by dividing the difference between weight-corrected Tc concentrations in whole sample and leach solution by the Tc concentration in dried feed. The Tc retention in heat-treated samples is given as the sum of soluble and insoluble Tc fractions, and was measured directly with NaOH fusion and LSC counting. The balance (100% minus Tc retention) represents the fraction of Tc volatilized. Figure 5 shows the fractions of Tc^{7+} and Tc^{4+} in each sample normalized to the Tc concentration in the dried feed, which was calculated by multiplying the

weight-corrected Tc concentration in the whole sample with the as-measured fraction of Tc^{7+} and Tc^{4+} in each sample determined by XANES analysis.

6 Discussion

Slow-cooling the heat-treated samples in the furnace presents a variation from previous studies with AN-102 simulated LAW with Re. The cooling rate of the furnace in question has not been quantitatively measured, but observation reveals that the temperature drops several hundred degrees in several minutes, and takes several hours to cool the final several hundred degrees to room temperature. Comparisons of pertechnetate and perrhenate retentions at 1000 °C show good agreement, suggesting that the additional time spent at the highest temperatures is limited enough to be immaterial. Future work with Tc crucible tests quenched in air are planned and will shine additional light on the effect of slow-cooling compared to air-quenching.

As shown in Table 4 and Figure 4, the final Tc retention after heat treatment to 1000°C can be improved by using reduced Tc sources— $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ or Tc-doped minerals—compared to the baseline KTcO_4 . Although there were no practical differences in final Tc retention at 1000°C between the feeds with $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ (52.7% retention) or Tc-doped minerals (53.1 to 57.9% retention), there were differences in the temperature dependencies of Tc valence and Tc partitioning into soluble and insoluble phases. This section discusses these differences in Tc behavior as a function of temperature to help understand the mechanism on how different Tc sources affect Tc volatilization/incorporation during early stages of feed melting processes.

For the dried feeds, Figure 4 and Figure 5 show that the KTcO_4 feed had ~100% Tc in the soluble phase as Tc^{7+} while the feeds with Tc-goethite and Tc-magnetite had 100% Tc in the

insoluble phase as Tc^{4+} , which would be expected. However, the two feeds with Tc-trevorite had ~20% of Tc in the soluble phase (18.2 to 22.8%) and ~10% of the total Tc as Tc^{7+} . The soluble Tc^{7+} found in the trevorite feeds is likely a result of partial oxidation of the trevorite particles during slurry preparation and drying. The feed with $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ had 14.3% Tc in the soluble phase and 23% as Tc^{7+} , suggesting that $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ oxidizes only partially to form soluble Tc^{7+} during slurry preparation and drying. This observation is different from the results reported by Kim et al. [29] who observed full oxidation of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ immediately after contact with simulated waste. It is likely that the difference was caused by different composition of simulated waste. In summary, more than 80% Tc for $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and Tc-trevorite feeds and 100% Tc for Tc-goethite and Tc-magnetite feeds stayed as insoluble Tc^{4+} through slurry preparation and drying. The better oxidation resistance of Tc-goethite during slurry preparation and drying is likely a result of the armoring mentioned in Section 2.5. The better resistance to oxidation of Tc-magnetite compared to Tc-trevorite is possibly due to the magnetite containing Fe^{2+} which may act as a sacrificial anode, delaying the oxidation of Tc^{4+} .

Only a small fraction of Tc (2.8 to 11.4%) was in the soluble phase for all samples heat treated to 800°C (Figure 4). As mentioned in Section 4.3, soluble Tc is not expected to be in the samples heat treated to 1000°C; therefore, leach tests were not performed for those samples. As shown in Figure 5, the samples heated to 800 and 1000°C contain ~100% Tc as Tc^{7+} by XANES, presumably in insoluble (glassy) phase for KTcO_4 , Tc-goethite, and Tc-magnetite.

As mentioned earlier, the important differences between feeds lie in the temperature dependencies of Tc valence and Tc partitioning into the soluble or insoluble phases especially in the samples heat treated to 600°C. We will first compare the results of the KTcO_4 feed with

KReO₄ feed in Jin et al. [5], and then discuss the effects of TcO₂·2H₂O and Tc-minerals on Tc behavior observed in the 600°C samples.

6.1 *KTcO₄ versus KReO₄*

Figure 6 compares the fractions of total un-volatilized Re and Tc as a function of heat treatment temperature for AN-102 feeds spiked with KReO₄ [5] and KTcO₄ (present study). In general, Re and Tc show similar trends for both insoluble and soluble phases. This result agrees with Matlack and Kim [25, 29] that Re is a good surrogate for Tc. One exception to this was the lower solubility of Tc at 800°C than for Re (Figure 6 bottom plot). It is possible that Tc experienced excess volatilization from the sulfate-rich salt phase at 800°C (see Darab and Smith [4]) during slow cooling in a hot furnace compared to air quenching used by Jin et al. [5].

6.2 *Effect of TcO₂·2H₂O*

As shown in Table 4 and Figure 4 for both feeds spiked with KTcO₄ and TcO₂·2H₂O, the samples heat treated to 600°C had the same normalized Tc concentration as the dried feeds-- that is, there was no volatile loss of Tc during heating to 600°C. Figure 7 shows the fractions of Tc added to the feed remaining in the insoluble and soluble phases as a function of heat treatment temperature for the two feeds. At 600°C, the TcO₂·2H₂O feed had slightly higher fraction of Tc in the insoluble phase (incorporated into the glass-forming melt) than the KTcO₄ feed. As shown in Figure 5, the TcO₂·2H₂O feed initially had 77% Tc as Tc⁴⁺ in the dried feed compared to 6% for the KTcO₄ feed, which may suggest that the difference in Tc valence states in the dried feeds affected how much Tc incorporated into the glassy phase at 600°C. However, the effect of Tc valence state on Tc volatilization could not be determined because there was no volatile loss of Tc up to 600°C for both feeds.

Figure 7 shows that the fraction of insoluble Tc increased more for the $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ feed than for the KTcO_4 feed from 600 to 800°C. There were only 3.4 and 2.8% of soluble Tc remaining at 800°C for $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and KTcO_4 , respectively. This indicates that during heating from 600 to 800°C, almost all Tc that did not become incorporated into the glass-forming melt volatilized. The fraction of total Tc volatilized during heating from 600 to 800°C was 48.9% for the KTcO_4 feed and 36.6% for the $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ feed while the fraction of Tc incorporated into glassy insoluble phase was 27.4% (bringing the total insoluble Tc to 48.3%) for the KTcO_4 feed and 34.7% (total insoluble Tc of 58.7%) for the $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ feed. Considering that 100% of the Tc was present as Tc^{7+} at 600°C for both feeds as shown in Figure 5, the valence state of Tc at 600°C is not wholly responsible for the difference between the fractions of Tc that volatilized or incorporated into the glass melt during heating from 600 to 800°C in these feeds.

6.3 Effect of Tc-minerals

Figure 8 shows the fraction of total Tc added to the feed remaining in the insoluble phase as a function of heat treatment temperature for the feeds spiked with various Tc-minerals compared to the feed with KTcO_4 . Similar to feeds with KTcO_4 and $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, all the feeds with Tc-minerals had no noticeable volatile loss of Tc during heating to 600°C (Figure 4), but there were differences in the fractions in the insoluble phase (Figure 8) and the degrees of oxidation (fraction of Tc^{7+} , Figure 5).

As shown in Figure 4 and Figure 5, the Tc-goethite sample had 92.8% of its initial Tc remaining at 600°C, with all of it as Tc^{4+} and 95.2% of it insoluble. Considering that the melting point of a typical goethite mineral is 350°C, the survival of 100% Tc^{4+} up to 600°C in the Tc-goethite feed is not understood although it could be a result of either the armoring process

discussed previously in Section 2.5 or transformation into hematite that occurs above about 230°C [30], which is shown to be energetically favorable [31]. According to Jin et al. [3-5], various fractions of mineral additives had already reacted by 600°C including ~50% of the quartz to form an early glass-forming melt. The glass formed at 600°C contained 22.9 % of the total Re in the KReO_4 feed [9] and 20.6 % of the total Tc in the KTcO_4 feed (see Figure 6 top plot). Although it is likely that a similar fraction of glass-forming melt was formed at 600°C in the Tc-goethite feed, the experimental and characterization methods used in the present study could not determine the split factors of insoluble Tc into Tc-minerals and the glassy phase. Two cases can be considered for the Tc-goethite feed at 600°C: 1) all Tc was still in Tc-goethite (i.e., there is no Tc incorporated into the glassy phase) or 2) a fraction of the Tc incorporated into the glassy phase, which implies the existence of Tc^{4+} in glassy phase. During heating from 600 to 800°C for the Tc-goethite feed, Tc retention decreased from 92.8% to 66.9%, and 95% of the Tc was Tc^{7+} at 800°C, with only 6% of Tc in the soluble phase; that is, almost all Tc remaining in the glassy phase was Tc^{7+} .

As shown in Figure 8, the feeds with Tc-magnetite and both Tc-trevorite had lower fractions of insoluble Tc (35.6 to 59.9%) compared to the feed with Tc-goethite (88.1%) in samples heat treated to 600°C. This trend agrees with the fraction of Tc^{4+} in the condensed phase; that is, 15 to 46% of the total Tc remaining as Tc^{4+} for the feeds with Tc-magnetite and both Tc-trevorite compared to 100% for the Tc-goethite feed heat treated to 600°C. Although the magnetite and trevorite phases with higher melting points should be more thermally stable than the goethite, the feed with Tc-goethite showed superior resistance to oxidation or melting reaction likely because of the armoring mentioned in Section 2.5. However, the different

temperature dependencies of the fractions of insoluble Tc and oxidized Tc^{7+} among three Tc-minerals is difficult to explain without detailed information on incorporation and distribution of Tc into mineral structure, especially on the mineral surface. Full characterization of the Tc-mineral phases was not pursued in the present study but is planned for selected Tc-minerals to better understand the mechanism that governs the effect of Tc-minerals on Tc incorporation into glass melt.

Based on current results, the effect of particle size is inconclusive. The Tc-trevorite phase was created by two methods, but neither was fully characterized. SEM imaging shows particle sizes apparently larger for the case of the Tc-trevorite from $\text{Fe}(\text{OH})_2$.

Based on observations from tests with four Tc-mineral feeds that 1) there was no noticeable Tc volatilization up to 600°C and 2) there was no soluble Tc remaining at 800°C , we believe that the balance of Tc not incorporated into insoluble glassy phase volatilized during heating from 600 to 800°C . This finding signifies that although there were large differences in the fraction of total Tc remaining as Tc^{4+} at 600°C (15 to 100%), they did not lead to a noticeable difference in the fraction of Tc volatilized during heating from 600 to 800°C .

6.4 Summary on the effect of reduced Tc sources

It is known that reducing conditions lead to lower volatile loss of Tc during vitrification because lower-valence Tc^{4+} compounds are less volatile than Tc^{7+} species such as pertechnetate [2, 4, 28]. The test results obtained during this study confirmed that the addition of Tc as Tc^{4+} compounds or Tc^{4+} minerals decreases Tc volatilization during crucible melting compared to Tc^{7+} pertechnetate. However, the results do not support the presumption that low volatility of the Tc^{4+} compounds is responsible for reduced Tc volatilization. This claim is primarily based on

the following two observations: 1) the $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ feed showed lower Tc volatilization during heating from 600 to 800°C than the KTcO_4 feed although both feeds had 100% Tc as Tc^{7+} at 600°C, and 2) the four feeds with Tc-minerals showed no noticeable difference in Tc volatilization during heating from 600 to 800°C although they all had different fractions of Tc^{4+} remaining at 600°C. In other words, Tc volatilization in the AN-102 feeds with various Tc sources tested in this study seems to be affected by factors other than the valence state of the Tc. The initial valence state of the Tc appears to cause some condition that effects volatility even after all the Tc is oxidized.

Jin et al. [5] proposed that the composition of soluble salt phases and partitioning of Re into these phases during melting play important roles in how Re becomes incorporated into the glassy phase up to ~800°C, above which no additional incorporation of Re was observed. Based on the results on Re partitioning as a function of temperature reported by Jin et al. [5], it can be assumed that the Tc-containing salt phase in the KTcO_4 feed is predominantly nitrate up to 600°C but then becomes dominated by sulfate as temperature increases to 700°C and above. The Tc in the KTcO_4 feed incorporates into the glass-forming melt or volatilizes while the Tc-containing molten salts react with other feed components. However, a common difference for the feeds with $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and Tc-mineral feeds compared to the KTcO_4 feed is that the Tc would incorporate into glass or volatilize while Tc-containing solids ($\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and Tc-minerals) react with either salt or early glass-forming melt that already formed at lower temperatures; in other words, there was a difference in reaction or reaction paths that accompany Tc incorporation or volatilization. Unlike the study by Jin et al. [5], the present study was not designed to investigate detailed reaction paths during the feed melting process because a

larger temperature interval was used and chemical analyses were performed for Tc only instead of all feed components.

7 Conclusion

The present crucible melting tests with a representative LAW feed spiked with KTcO_4 showed that Tc and Re have similar behaviors in terms of volatilization and incorporation into glass phase during early stages of feed melting. This finding is consistent with previous results showing that Re is a good Tc surrogate under oxidizing conditions. The test results of the feeds spiked with reduced forms of Tc showed that the addition of Tc as $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and various Tc^{4+} -minerals decreased Tc volatilization during crucible melting compared to Tc^{7+} pertechnetate. However, results from the present do not support the presumption that low volatility of the Tc^{4+} compounds is responsible for reduced Tc volatilization. We postulate that other factors not related to Tc valence state, such as different reaction paths that accompany Tc incorporation or volatilization, are likely important. Additional studies are needed to investigate the effect Tc-minerals on partitioning and distribution of Tc during melting of simulated LAW glass feeds and their effect on Tc incorporation into and volatilization from glass melt.

8 Acknowledgment

The authors gratefully acknowledge the financial support provided by William F. Hamel, Jr., Federal Project Director, of the U.S. Department of Energy (DOE) Waste Treatment and Immobilization Plant Project. Pacific Northwest National Laboratory is operated by Battelle for DOE under contract DE-AC05-76RL01830. XANES spectroscopy and analysis was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Chemical

Sciences, Biosciences, and Geosciences Division (CSGB), Heavy Element Chemistry Program and was performed at Lawrence Berkeley National Laboratory under contract No. DE-AC02-05CH11231. Tc K-edge XAFS spectra were obtained at the Stanford Synchrotron Radiation Lightsource (SSRL), SLAC National Accelerator Laboratory, which is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515.

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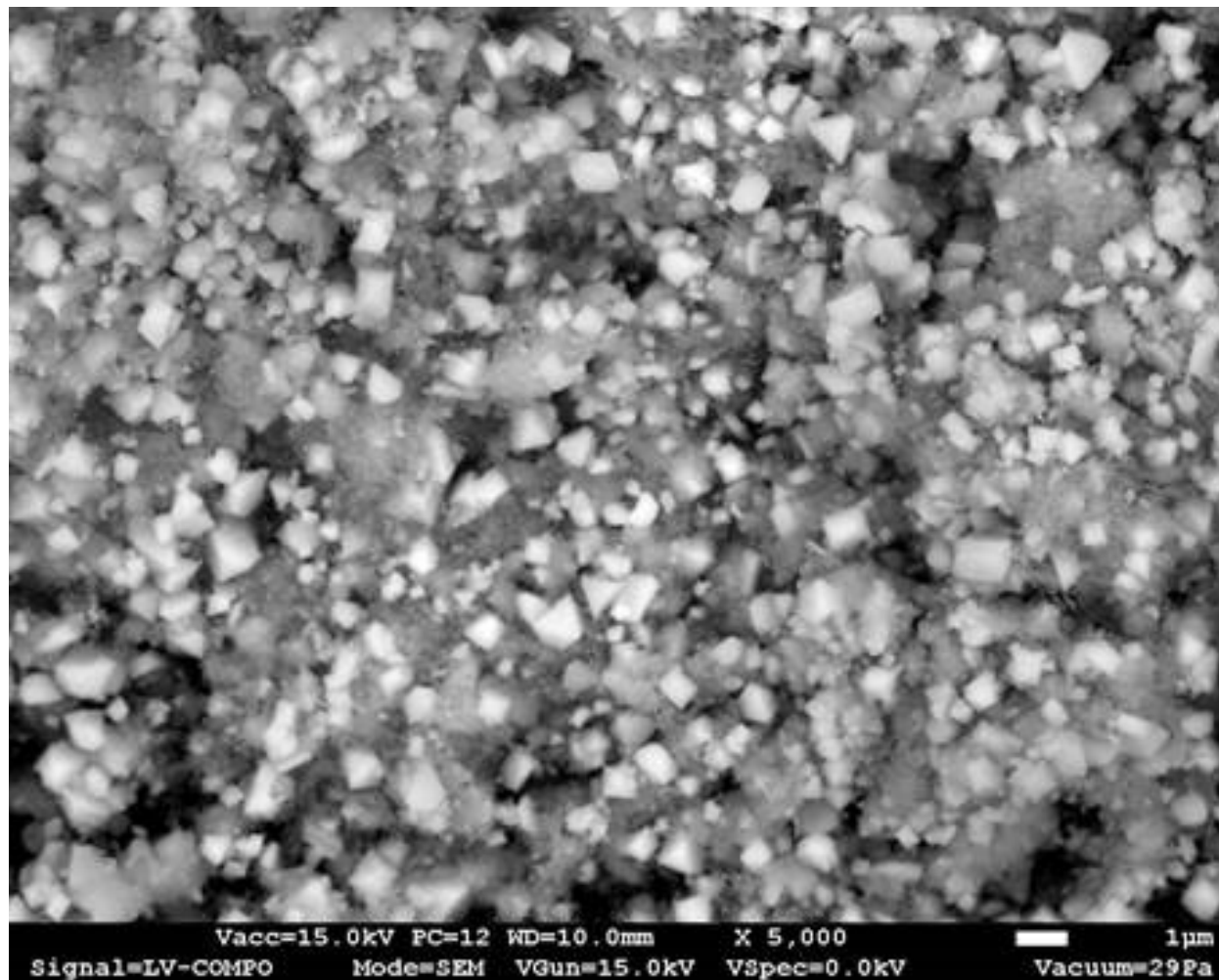
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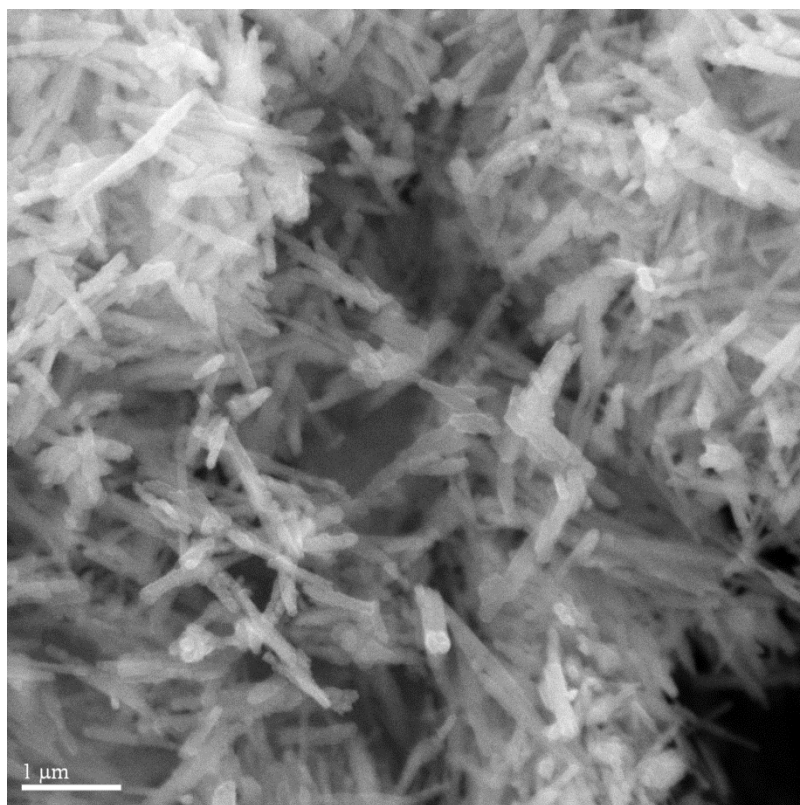


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516 Figure 1. Tc-trevorite from Fe(OH)₂ by SEM

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520 **Figure 2. Tc-goethite by SEM**

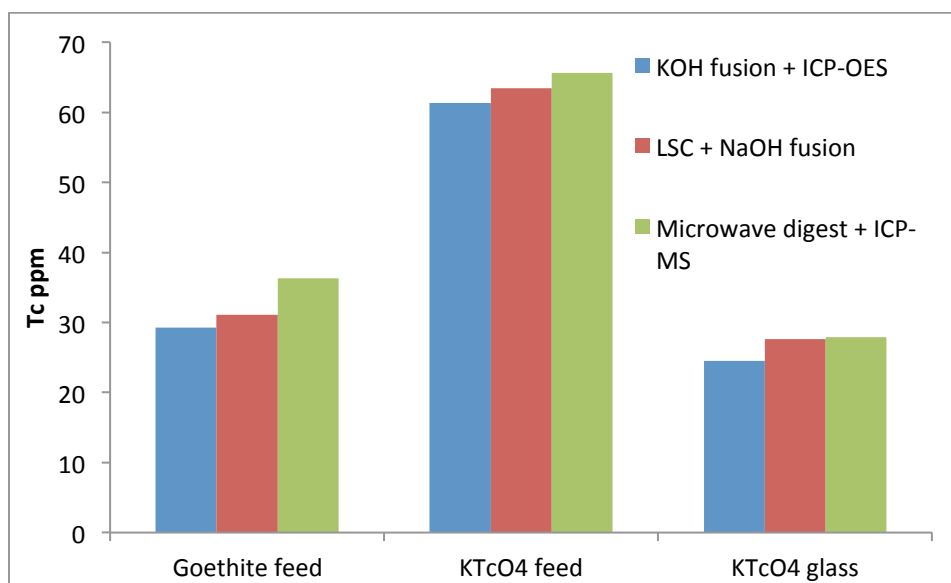
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527 **Figure 3. Comparative analyses of three powdered samples by KOH fusion and ICP-MS analysis by**
528 **SwRI, NaOH fusion and LSC at PNNL, and microwave digestion and ICP-MS analysis at PNNL.**

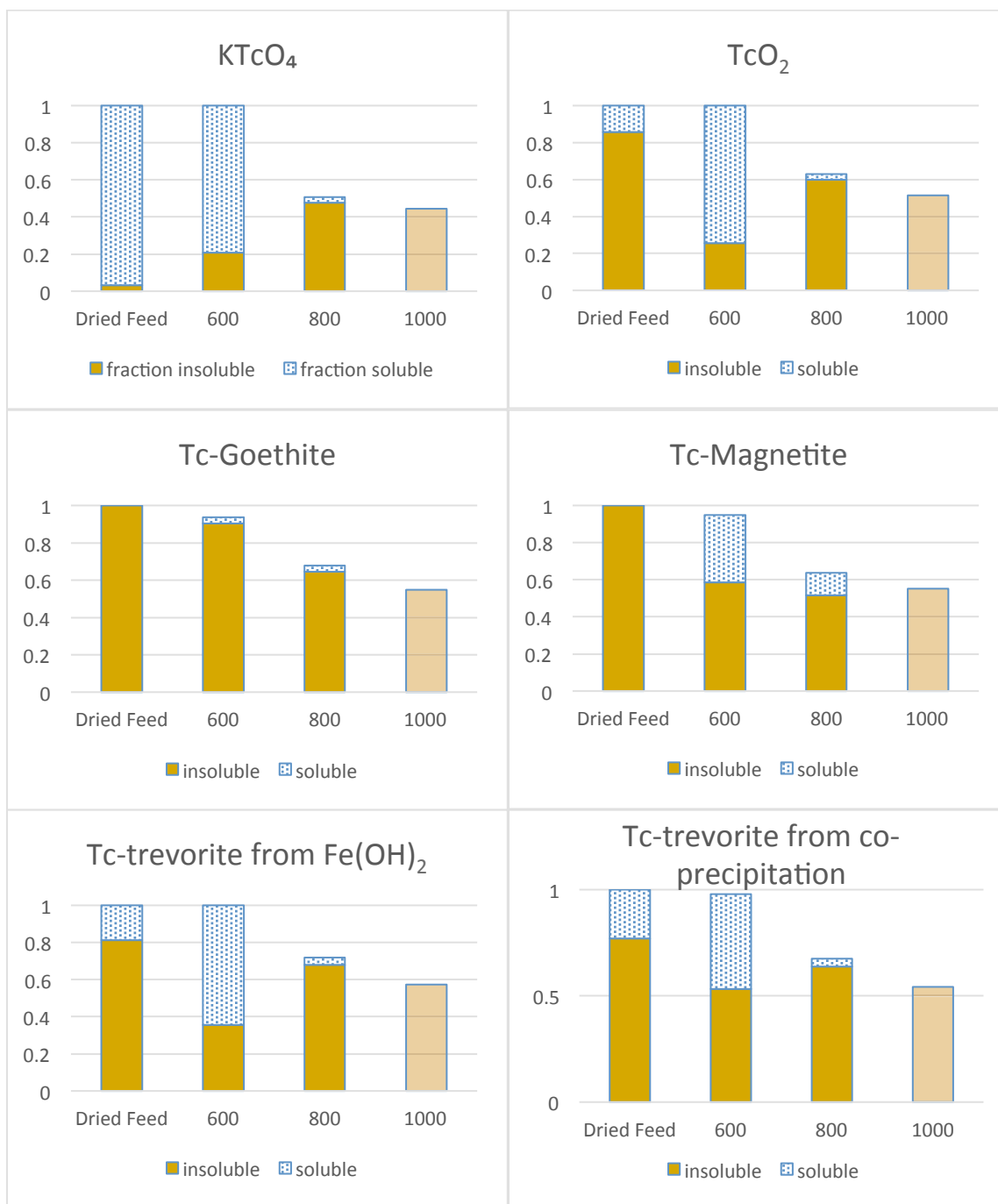
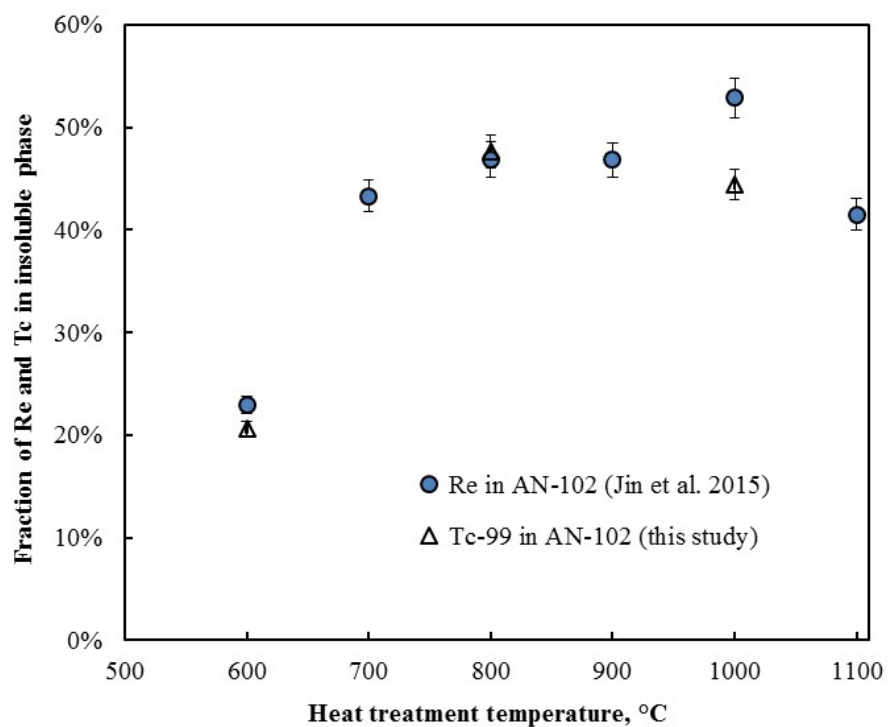


Figure 4. Normalized results of leach tests and LSC on AN-102 feeds doped with six different Tc sources in dried feed and heat treated to various temperatures. Y-axis is Tc concentration normalized to the total concentration in dried feed. Blue portions of bars indicate the concentrations of Tc found in each sample by leaching. Brown solid portions of bars indicate the total Tc concentration minus the leached Tc concentration. Transparent data at 1000°C are assumed to be fully insoluble but were not measured by leach tests.

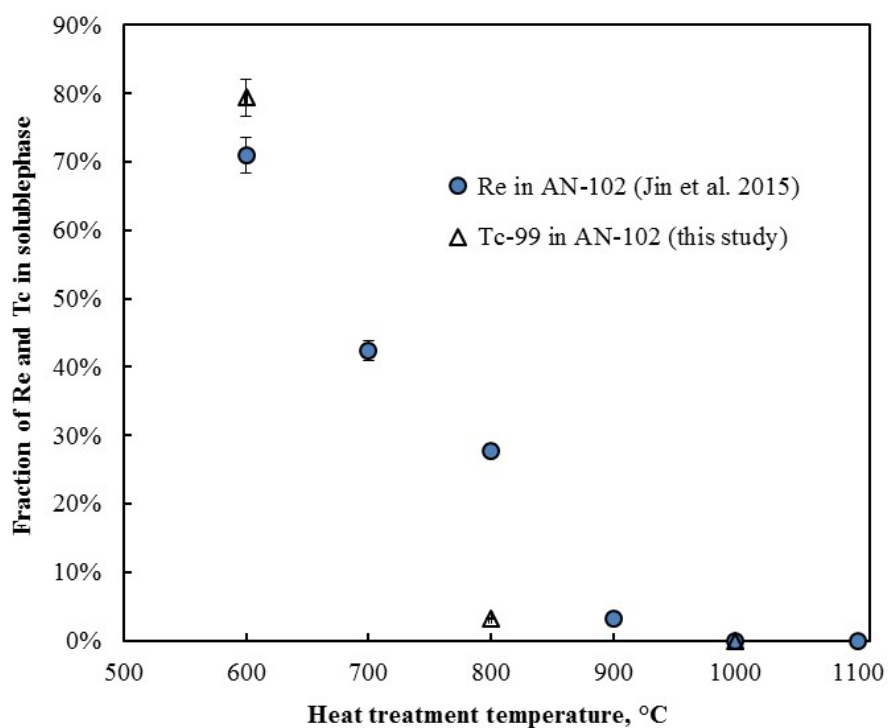


Figure 5. XANES analysis of Tc in feeds doped with six Tc sources in dried feed and heat treated to various temperatures. Black shaded columns indicate the Tc^{4+} fraction detected by XANES. The orange columns indicate the fraction of Tc^{7+} detected by XANES. Transparent column were not measured and are assumed to be fully Tc^{7+} .

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549 **Figure 6. Fractions of total Re and Tc remained in the insoluble (top plot) and soluble (bottom plot)**
 550 **phases of the heat-treated samples as a function of temperature. The error bars represent the**
 551 **standard deviation of chemical analyses with RSD = 3.6% for Re (from Jin et al. 2015 [5]) and 3.4% for**
 552 **Tc (Table 2).**

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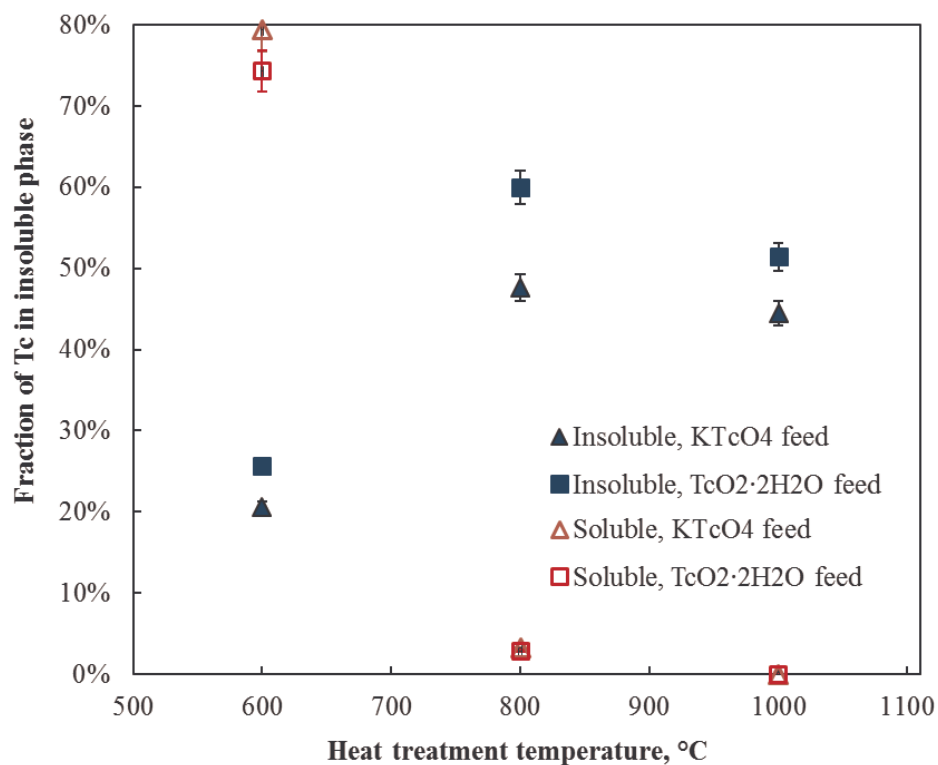


Figure 7. Fraction of total Tc-99 remained in the insoluble and soluble phases of the heat-treated samples as a function of temperature for the feeds with KTcO₄ and TcO₂·2H₂O. The error bars represent the standard deviation of chemical analyses with RSD = 3.4% (Table 2).

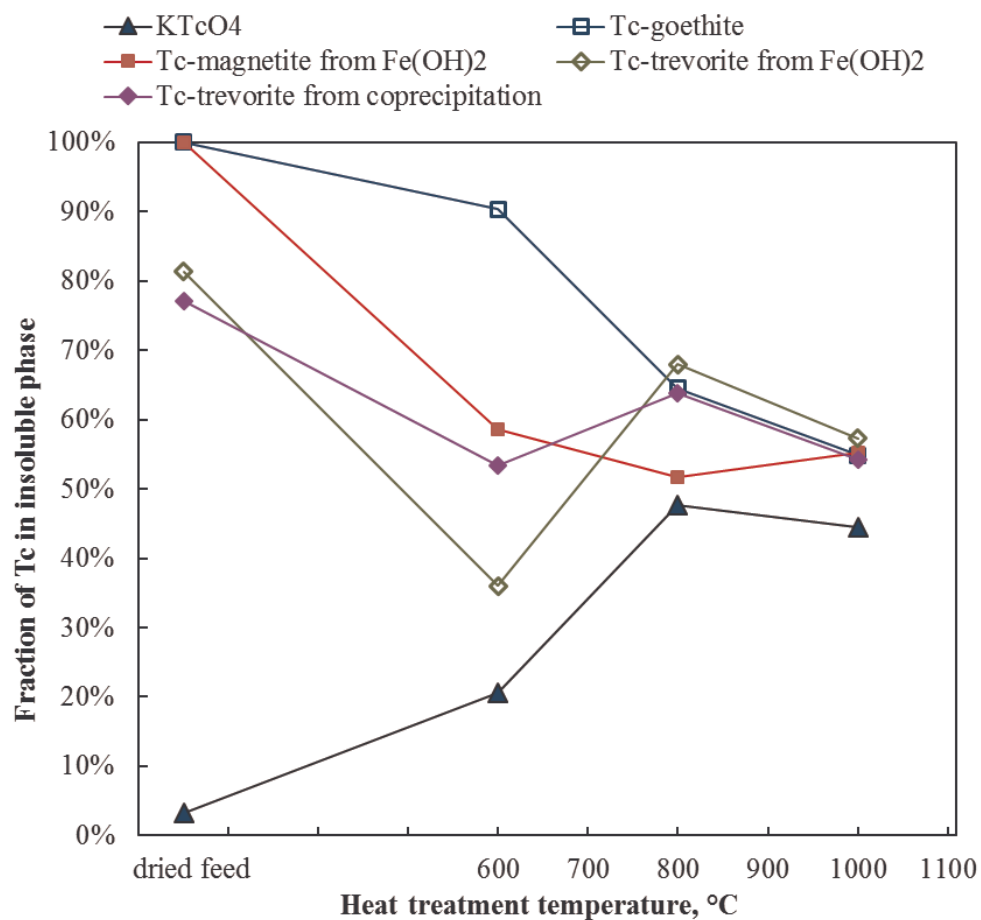


Figure 8. Fraction of total Tc-99 remained in the insoluble phase of the heat-treated samples for the feeds with minerals compared to the KTcO_4 feed as a function of temperature. The error bars were not included to avoid the plot being too cluttered. Duplicate leach tests for feeds showed relative percent differences between 0.77% and 4.24% when testing for water-soluble Tc.

565 **11 Tables**

566 **Table 1. Composition of AN-102 Glass Feed to make 1 Liter slurry [25]**

Material	
Simulated waste	g/l
Al(NO ₃) ₃ ·9H ₂ O, 60% sol.	142.07
H ₃ BO ₃	0.11
Ca(NO ₃) ₂ ·4H ₂ O	1.47
Na ₂ CrO ₄ ·4H ₂ O	2.78
KOH	8.12
NaOH, 50% sol. D=1.53	102.73
NiO	0.09
PbO	0.09
SiO ₂	0.1
NaCl	3.74
NaF	1.99
Na ₃ PO ₄ ·12H ₂ O	7.56
Na ₂ SO ₄	12.2
NaNO ₂	65.13
NaNO ₃	94.65
Na ₂ CO ₃	48.96
Sodium Formate (C1)	24.91
Sodium Oxalate (C2)	1.44
Glycolic Acid (C2)	30.22
Citric Acid (C6)	9.07
Target Glass Weight	1145.23
Total Simulant Weight	1246.58
Kyanite (Al ₂ SiO ₅) 325 Mesh (Kyanite Mining) (g)	96.64
H ₃ BO ₃ (US Borax – Technical Granular) (g)	200.67
Wollastonite NYAD 325 Mesh (NYCO Minerals) (g)	158.24
Fe ₂ O ₃ (97% Alfa) (g)	59.21
Li ₂ CO ₃ (Chemetall Foote Co. Technical grade) (g)	90.77
Olivine (Mg ₂ SiO ₄) 325 Mesh (#180 Unimin) (g)	33.18
SiO ₂ (Sil-co-Sil 75 US Silica) (g)	358.02
TiO ₂ (Rutile Airfloated Chemaloy) (g)	16.75
ZnO (KADOX – 920 Zinc Corp. of America) (g)	39.63
Zircon ZrSiO ₄ (Flour) Mesh 325 (AM. Mineral) (g)	51.13
Measured Simulant Weight for 1 liter (g)	1247

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569 **Table 2. Summary of results for Tc concentrations by LSC, weight-loss factor after 1000°C heat**
 570 **treatment, and calculated Tc retention from K₂TcO₄-spiked original and duplicate feed batches**

Feed batch	Tc concentration (ppm)		Weight-loss factor	Tc retention
	Pre-heat treatment	Post-heat treatment (weight corrected)		
Original	63.4	27.6	0.819	0.436
Duplicate	63.0	28.3	0.813	0.448
Duplicate	63.0	27.8	0.813	0.441
Duplicate	62.5	26.1	0.812	0.418
RSD	0.6%	3.4%		

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RSD: relative standard deviation

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573 **Table 3. Comparison of three analytical methods for Tc concentrations in selected feed and heat-**
 574 **treated samples**

Analytical method	Goethite feed	K ₂ TcO ₄ feed	K ₂ TcO ₄ 1000°C heat treated (weight corrected)
ICP-MS after KOH fusion (SwRI)	29.3	61.3	24.5
LSC after NaOH fusion	31.1	63.4(0.37)*	27.6(0.95)*
ICP-MS after microwave-assisted digestion	36.3	65.6	27.9

575 *Number in parenthesis is standard deviation calculated from RSD value given in Table 2

576

Table 4. Sumamry of rsults for Tc concentrations by LSC, weith loss factors, and Tc valences by XANES and calculated values for Tc retention and fraction of soluble Tc

Tc source	HT temp. (°C)	Tc conc. (ppm)		Weight-loss factor	Tc retention after HT	XANES results	
		In whole sample	In leach solution*			Fraction of Tc ⁷⁺	Fraction of Tc ⁴⁺
KTcO ₄	Dried feed	63.4	61.5	NA	NA	0.94±0.06	0.06±0.05
	600	63.4	50.2	0.886	1.000	1.00±0.02	0.00±0.01
	800	32.4	1.8	0.819	0.511	1.00±0.03	0.00±0.03
	1000	27.6	NM	0.819	0.436	1.00±0.04	0.00±0.03
Tc Goethite	Dried feed	31.1	0.1	NA	NA	0.00±0.04	1.00±0.03
	600	28.9	1.5	0.891	0.928	0.00±0.04	1.00±0.03
	800	20.8	1.3	0.811	0.669	0.95±0.04	0.05±0.04
	1000	16.5	NM	0.812	0.531	0.99±0.04	0.01±0.04
Tc Magnetite from Fe(OH) ₂	Dried feed	57.8	0.5	NA	NA	0.00±0.03	1.00±0.02
	600	55.4	20.8	0.886	0.959	0.54±0.02	0.46±0.02
	800	37.5	6.6	0.812	0.649	1.00±0.02	0.00±0.01
	1000	32.3	NM	0.802	0.559	0.97±0.04	0.03±0.03
Tc-trevorite from Fe(OH) ₂	Dried feed	74.9	13.6	NA	NA	0.10±0.03	0.90±0.03
	600	75.8	49.1	0.871	1.000**	0.66±0.04	0.34±0.04
	800	53.7	2.6	0.800	0.717	NM	NM
	1000	43.3	NM	0.821	0.579	NM	NM
Tc- trevorite from co-precipitation	Dried feed	104.9	23.9	NA	NA	0.10±0.03	0.90±0.04
	600	103.4	47.0	0.864	0.986	0.85±0.03	0.15±0.04
	800	71.4	4.1	0.787	0.681	NM	NM
	1000	57.5	NM	0.815	0.548	NM	NM
TcO ₂ •2H ₂ O	Dried feed	34.9	5.0	NA	NA	0.23***	0.77***
	600	34.5	26.1	0.870	0.989	0.96±0.04	0.00±0.06
	800	21.7	1.2	0.806	0.622	NM	NM
	1000	18.4	NM	0.816	0.527	NM	NM

*weight corrected to the dried feed for heat-treated samples

**assumed value (Tc concentration in 600C sample was slightly higher than in dried feed)

***XANES analysis fitted several percentage of Tc¹⁺, which has been disregarded and Tc⁴⁺ and Tc⁷⁺ have been normalized to 1.

HT: heat treatment, NM: not measured, NA: not applicable